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(54) Title:	A DETERGENT COMPOSITION	
(57) Abstract	<p>The present invention relates to detergent compositions comprising anionic midbranched surfactant, low levels of a builder system and an alkalinity system comprising carbonate salts. The compositions are particularly useful as solid laundry detergent compositions.</p>	

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A Detergent CompositionTechnical Field

The present invention relates to detergent compositions comprising anionic mid-branched surfactant, low levels of a builder system and an alkalinity system comprising carbonate salts. The compositions are particularly useful as solid laundry detergent compositions.

Background to the Invention

Recently, a certain new type of anionic mid-chain branched surfactants has been developed. These surfactants are described in unpublished co-pending applications US 97/06485, US 97/06474, US 97/06339, US 97/06476 and US 97/06338.

Hard water conditions, due to the presence of Ca and Mg ions in the washing water and on the fabrics, can cause a reduction of the performance of the various components in detergents, especially charged surfactants, such as anionic surfactants. Therefor, builders are traditionally employed in detergent compositions, to build the Ca and Mg ions, thereby softening the water. A disadvantage of high levels of builders, however, is that many of these builders are not water-soluble, or only partially water soluble. This can result in a poor solubility of the detergent in the washing water and it can lead to deposition of builder material on the washed fabrics and/ or on the (dish) washing machine, resulting in for example greying of the fabrics. Furthermore, the use of high levels of builder materials can be very expensive.

It has now surprisingly been found that these specific mid-chain branched surfactants have an excellent surfactancy and cleaning performance under (severe) hard water conditions. Furthermore, it has surprisingly been found that detergent compositions comprising these mid-chain branched surfactants and only very low amount of builder have an excellent cleaning performance. It also has been found

that the mid-chain branched surfactants perform better in an (slightly) alkaline environment. However, the reduction in detergent compositions, containing these mid-chain branched surfactants, of the levels of builder material, which are known sources of alkalinity in detergent compositions, leads to a less alkaline environment. To compensate for this, the inventors have found that the introduction in detergent compositions of small amount of an alkalinity source, preferably carbonate salts, can deliver the required alkalinity for an optimum performance of the mid-chain branched surfactants, whilst allowing the reduction of the levels of builder materials

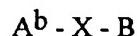
An additional benefit is that the reduction of the levels of builder material in the detergent compositions leads to a reduction of formulation cost.

All documents cited are hereby incorporate herein by reference.

Summary of the Invention

The invention relates to solid detergent compositions having a density of from 330 grams/litre to 1400 grams/litre, comprising

a) at least 0.5%, preferably at least 5%, more preferably at 10% by weight of the composition of a surfactant system, comprising longer alkyl chain, mid-chain branched surfactant compounds of the formula:



wherein:

(I) A^b is a hydrophobic mid-chain branched alkyl moiety, having in total 9 to 22 carbons in the moiety, preferably from 12 to about 18, having: (1) a longest linear carbon chain attached to the $-X-B$ moiety in the range of from 8 to 21 carbon atoms; (2) one or more C_1-C_3 alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of the position 2 carbon, counting from position 1 carbon (#1) which is attached to the $-X-B$ moiety, to the position of the terminal carbon minus 2 carbons, (the ($\omega - 2$) carbon); and (4) when more than one of these compounds is present, the average total number of carbon

atoms in the A^b-X moieties in the above formula is within the range of greater than 14.5 to about 18, preferably from about 15 to about 17;

(II) B is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, preferably polyoxyethylene and polyoxypropylene, alkoxylated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polygluconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccinates, polyalkoxylated carboxylates, glucamides, taurinates, sarcosinates, glycinate, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxylated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkylated/polyhydroxyalkylated quats, alkylated quats, alkylated/polyhydroxylated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and

(III) X is selected from -CH₂- and -C(O)-; and

b) from 0.5% to 25% by weight of the composition a builder system; and

c) from 0.0% to 50% by weight of the composition of an alkalinity system comprising carbonate salts,

with the proviso that when system a) is present at a level of 3% by weight and system b) is present at a level of 19% by weight, the alkalinity system c) does not comprise 8% by weight of sodium carbonate.

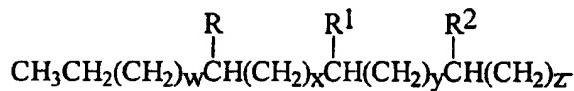
Preferably, the surfactant system a) comprises mid-chain branched primary alkyl sulfate or sulfonate surfactants.

Detailed Description of the Invention

Mid-Chain Branched Surfactant Compounds-Containing Surfactant System

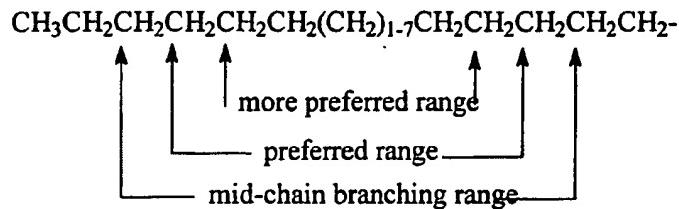
The detergent compositions of the invention comprise at least 0.5%, preferably at least 5%, more preferably at least 10% by weight of the composition of a surfactant system, comprising longer alkyl chain, mid-chain branched surfactant compounds, selected from the group consisting of surfactant compounds having the formula as defined above.

Preferred surfactant systems herein comprise longer alkyl chain, mid-chain branched surfactant compounds of the above formula wherein the A^b moiety is a branched primary alkyl moiety having the formula:



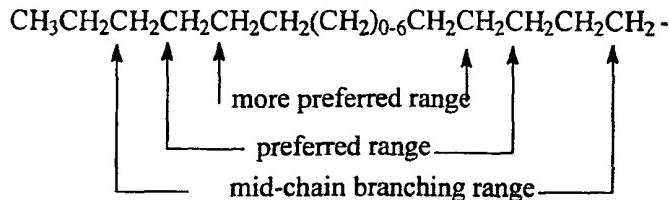
wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula (including the R, R¹, and R² branching) is from 13 to 19; R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl (preferably methyl), provided R, R¹, and R² are not all hydrogen and, when z is 0, at least R or R¹ is not hydrogen; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer from 0 to 13; and w + x + y + z is from 7 to 13.

In general, for the mid-chain branched surfactant compounds of the surfactant system, certain points of branching (e.g., the location along the chain of the R, R¹, and/or R² moieties in the above formula) are preferred over other points of branching along the backbone of the surfactant. The formula below illustrates the mid-chain branching range (i.e., where points of branching occur), preferred mid-chain branching range, and more preferred mid-chain branching range for mono-methyl branched alkyl A^b moieties useful according to the present invention.



It should be noted that for the mono-methyl substituted surfactants these ranges exclude the two terminal carbon atoms of the chain and the carbon atom immediately adjacent to the -X - B group.

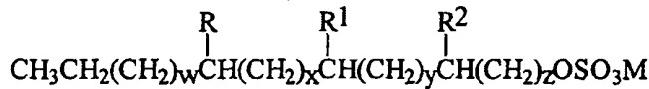
The formula below illustrates the mid-chain branching range, preferred mid-chain branching range, and more preferred mid-chain branching range for di-methyl substituted alkyl A^b moieties useful according to the present invention.



Preferred are surfactant compounds wherein in the above formula the A^b moiety does not have any quaternary substituted carbon atoms (i.e., 4 carbon atoms directly attached to one carbon atom).

The most preferred mid-chain branched surfactants compounds for use in the detergent compositions herein are mid-chain branched primary alkyl sulfonate and, even more preferably, sulfate surfactants.

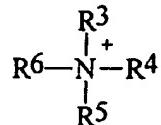
Preferred mid-chain branched primary alkyl sulfate surfactants are of the formula



These surfactants have a linear primary alkyl sulfate chain backbone (i.e., the longest linear carbon chain which includes the sulfated carbon atom) which preferably comprises from 12 to 19 carbon atoms and their branched primary alkyl moieties comprise preferably a total of at least 14 and preferably no more than 20, carbon atoms. In the surfactant system comprising more than one of these sulfate surfactants, the average total number of carbon atoms for the branched primary alkyl moieties is preferably within the range of from greater than 14.5 to about 17.5. Thus, the surfactant system preferably comprises at least one branched primary alkyl sulfate surfactant compound having a longest linear carbon chain of not less than 12 carbon atoms or not more than 19 carbon atoms, and the total number of carbon atoms including branching must be at least 14, and further the average total number of carbon atoms for the branched primary alkyl moiety is within the range of greater than 14.5 to about 17.5.

R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl group (preferably hydrogen or C₁-C₂ alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R, R¹, and R² are not all hydrogen. Further, when z is 1, at least R or R¹ is not hydrogen.

M is hydrogen or a salt forming cation depending upon the method of synthesis. Examples of salt forming cations are lithium, sodium, potassium, calcium, magnesium, quaternary alkyl amines having the formula



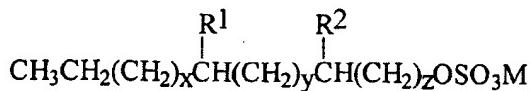
wherein R³, R⁴, R⁵ and R⁶ are independently hydrogen, C₁-C₂₂ alkylene, C₄-C₂₂ branched alkylene, C₁-C₆ alkanol, C₁-C₂₂ alkenylene, C₄-C₂₂ branched alkenylene, and mixtures thereof. Preferred cations are ammonium (R³, R⁴, R⁵ and R⁶ equal hydrogen), sodium, potassium, mono-, di-, and trialkanol ammonium, and mixtures thereof. The monoalkanol ammonium compounds of the present invention have R³ equal to C₁-C₆ alkanol, R⁴, R⁵ and R⁶ equal to hydrogen; dialkanol ammonium compounds of the present invention have R³ and R⁴ equal to C₁-C₆ alkanol, R⁵ and R⁶ equal to hydrogen; trialkanol ammonium compounds of the present invention have R³, R⁴ and R⁵ equal to C₁-C₆ alkanol, R⁶ equal to hydrogen. Preferred alkanol ammonium salts of the present invention are the mono-, di- and tri- quaternary ammonium compounds having the formulas:



Preferred M is sodium, potassium and the C₂ alkanol ammonium salts listed above; most preferred is sodium.

Further regarding the above formula, w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer of at least 1; and w + x + y + z is an integer from 8 to 14.

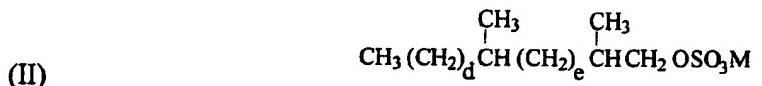
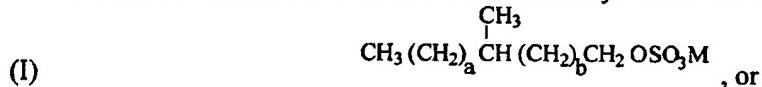
Another preferred surfactant system of the present invention have one or more branched primary alkyl sulfates having the formula



wherein the total number of carbon atoms, including branching, is from 15 to 18, and when more than one of these sulfates is present, the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than 14.5 to about 17.5; R¹ and R² are each independently hydrogen or C₁-C₃ alkyl; M is a water soluble cation; x is from 0 to 11; y is from 0 to 11; z is at least 2; and x + y + z is from 9 to 13; provided R¹ and R² are not both hydrogen.

Preferably, the surfactant system comprises at least 20% by weight of the system, more preferably at least 60% by weight, even more preferably at least 90% by weight of the system, of mid-chain branched primary alkyl sulfates, preferably having R¹ and R² independently hydrogen or methyl, provided R¹ and R² are not both hydrogen; x + y is equal to 8, 9, or 10 and z is at least 2, whereby the average total number of carbon atoms in these sulfate surfactants is preferably from 14 to 18, more preferably from 15 to 17, even more preferably from 16 to 17.

Furthermore, preferred surfactant systems are those, which comprise at least about 20%, more preferably at least 60%, even more preferably at least 90% by weight of the system, of one or more mid-chain branched alkyl sulfates having the formula:



or mixtures thereof; wherein M represents one or more cations; a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8; when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9; when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10; when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11; when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12; when a + b = 15, a is an integer from 2 to 14 and b is an integer from 1 to 13; when a + b = 16, a is an integer from 2 to 15 and b is an integer from 1 to 14; when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6; when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7;

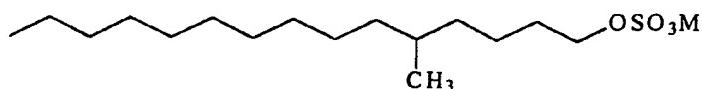
when $d + e = 10$, d is an integer from 2 to 9 and e is an integer from 1 to 8;
when $d + e = 11$, d is an integer from 2 to 10 and e is an integer from 1 to 9;
when $d + e = 12$, d is an integer from 2 to 11 and e is an integer from 1 to 10;
when $d + e = 13$, d is an integer from 2 to 12 and e is an integer from 1 to 11;
when $d + e = 14$, d is an integer from 2 to 13 and e is an integer from 1 to 12;
whereby, when more than one of these sulfate surfactants is present in the surfactant system, the average total number of carbon atoms in the branched primary alkyl moieties having the above formulas is within the range of greater than 14.5 to about 17.5.

Preferred mono-methyl branched primary alkyl sulfates are selected from the group consisting of: 3-methyl pentadecanol sulfate, 4-methyl pentadecanol sulfate, 5-methyl pentadecanol sulfate, 6-methyl pentadecanol sulfate, 7-methyl pentadecanol sulfate, 8-methyl pentadecanol sulfate, 9-methyl pentadecanol sulfate, 10-methyl pentadecanol sulfate, 11-methyl pentadecanol sulfate, 12-methyl pentadecanol sulfate, 13-methyl pentadecanol sulfate, 3-methyl hexadecanol sulfate, 4-methyl hexadecanol sulfate, 5-methyl hexadecanol sulfate, 6-methyl hexadecanol sulfate, 7-methyl hexadecanol sulfate, 8-methyl hexadecanol sulfate, 9-methyl hexadecanol sulfate, 10-methyl hexadecanol sulfate, 11-methyl hexadecanol sulfate, 12-methyl hexadecanol sulfate, 13-methyl hexadecanol sulfate, 14-methyl hexadecanol sulfate, and mixtures thereof.

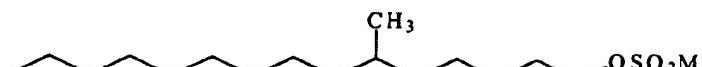
Preferred di-methyl branched primary alkyl sulfates are selected from the group consisting of: 2,3-methyl tetradecanol sulfate, 2,4-methyl tetradecanol sulfate, 2,5-methyl tetradecanol sulfate, 2,6-methyl tetradecanol sulfate, 2,7-methyl tetradecanol sulfate, 2,8-methyl tetradecanol sulfate, 2,9-methyl tetradecanol sulfate, 2,10-methyl tetradecanol sulfate, 2,11-methyl tetradecanol sulfate, 2,12-methyl tetradecanol sulfate, 2,3-methyl pentadecanol sulfate, 2,4-methyl pentadecanol sulfate, 2,5-methyl pentadecanol sulfate, 2,6-methyl pentadecanol sulfate, 2,7-methyl pentadecanol sulfate, 2,8-methyl pentadecanol sulfate, 2,9-methyl pentadecanol sulfate, 2,10-methyl pentadecanol sulfate, 2,11-methyl pentadecanol sulfate, 2,12-methyl pentadecanol sulfate, 2,13-methyl pentadecanol sulfate, and mixtures thereof.

The following branched primary alkyl sulfates comprising 16 carbon atoms and having one branching unit are examples of preferred branched surfactants useful in the present invention compositions:

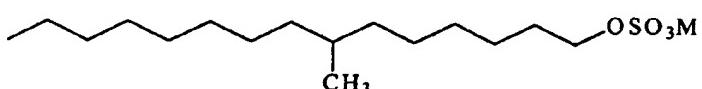
5-methylpentadecylsulfate having the formula:



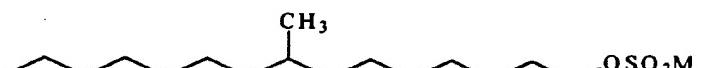
6-methylpentadecylsulfate having the formula



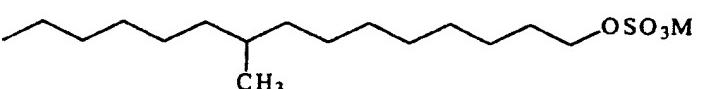
7-methylpentadecylsulfate having the formula



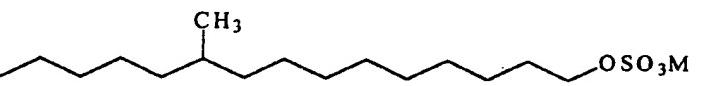
8-methylpentadecylsulfate having the formula



9-methylpentadecylsulfate having the formula



10-methylpentadecylsulfate having the formula

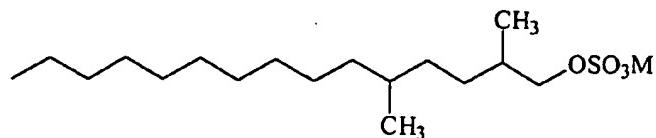


wherein M is preferably sodium.

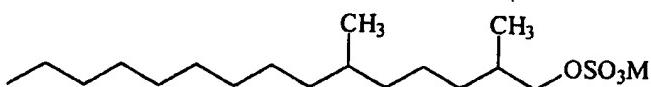
The following branched primary alkyl sulfates comprising 17 carbon atoms and having two branching units are examples of preferred branched surfactants according to the present invention:

2,5-dimethylpentadecylsulfate having the formula:

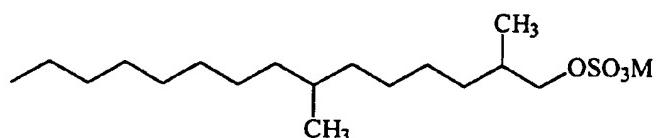
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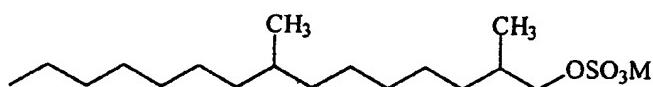
2,6-dimethylpentadecylsulfate having the formula



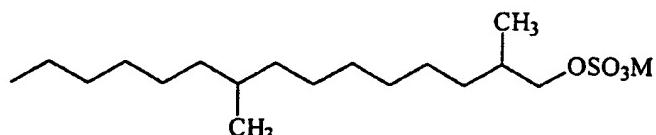
2,7-dimethylpentadecylsulfate having the formula



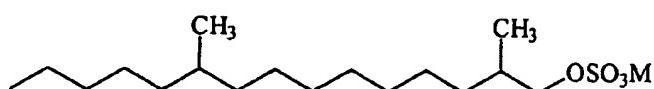
2,8-dimethylpentadecylsulfate having the formula



2,9-dimethylpentadecylsulfate having the formula



2,10-dimethylpentadecylsulfate having the formula



wherein M is preferably sodium.

Builder system

The detergent compositions of the invention comprise of from 0.5% to 25% by weight of a builder system, preferably from 1.0% to 20%, more preferably from 5% to 18%, even more preferred from 8% to 18% by weight of the detergent composition.

Both water-soluble and partially water-soluble or water-insoluble builder compounds can be comprised in the builder system of the present invention

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts. Preferably, the polycarboxylic acids or their salts comprise at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder or its salt can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates or their acids containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates or their acids containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates or their acids containing three carboxy groups include, in particular, water-soluble citrates, aconitlates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447. The most preferred polycarboxylic acid containing three carboxy groups is citric acid, mono-hydrate anhydrous or optionally in a liquid form, preferably present at a level of from 0.1% to 15%, more preferably from 0.5% to 8% by weight of the composition.

Polycarboxylates or their acids containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates or their acids containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates or their acids are hydroxycarboxylates or acids containing up to three carboxy groups per molecule, more particularly citrates or citric acid, as described above.

It should be understood that the parent acids of the monomeric or oligomeric polycarboxylate or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder compounds for the builder system of the invention.

Organic polymeric compounds are preferred builder compounds of the builder system of the detergent composition in accord with the invention, and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric builder compound, it is meant herein essentially any polymeric organic compound commonly used as builder, dispersant, and anti-redeposition and soil suspension agent in detergent, not being a polymeric or oligomeric (poly)carboxylate compound described above.

Organic polymeric compound is typically incorporated in the builder system of the invention at a level of from 0.1% to 50%, preferably from 0.5% to 35%, most preferably from 1% to 20% by weight of the builder system.

Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid/ maleic anhydride. The average molecular weight of such copolymers in the acid form preferably can range from 1,000 to 100,000, more preferably from 2,000 to 75,000 or even more preferred to 70,000, but most preferred are the co-polymers with a average molecular weight of from 2,500 to 20,000 or in another preferred embodiment from 60,000 to 75,000 or even 70,000. The ratio of acrylate to maleate segments in such copolymers will generally range from 30:1 to 1:30, more preferably from 10:1 to 1:1, most preferably from 4:1 to 7:3. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble

acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986.

Other suitable polymeric carboxylate-containing builder compounds can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are for example the water-soluble salts of polymerized acrylic acid. The average molecular weight of such homo-polymers in the acid form preferably ranges from 1,800 to 100,000, more preferably from 2,000 to 10,000, most preferably from 3,000 to 5,000. Water-soluble salts of such acrylic acid polymers or can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Also polyamino-based compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

A further example of polymeric carboxylate-containing builder compounds suitable for the purpose of the invention include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Terpolymers containing monomer units selected from maleic acid, acrylic acid and polyaspartic acid, particularly those having an average molecular weight of from 5,000 to 20,000, are also suitable herein.

Further useful polymeric carboxylate-containing builder compounds are the polyelectrolyte-containing glycols, particularly those of molecular weight 1,000-10,000, more particularly 2,000 to 8,000 and most preferably about 4,000.

Other preferred polymeric carboxylate-containing builder compounds are those which typically have a hydrophilic backbone and at least one hydrophobic side chain.

Preferably this type of polymeric carboxylate-containing builder compounds have a molecular weight of between 500 and 100,000, more preferred from 1,000 to 70,000, especially preferred from 1,500 to 10,000, or in another preferred embodiment from 2,800 to 6,000. Polymeric carboxylate-containing builder compounds for use herein may for example be prepared by using conventional aqueous polymerisation procedures, suitable methods are for example described in GB 89 24477, GB 89 24478 and GB 89 24479.

Generally the hydrophilic backbone of the polymer is predominantly linear (the main chain of the backbone constitutes at least 50%, preferably more than 75%, most preferred more than 90% by weight of the backbone), suitable monomer constituents of the hydrophilic backbone are for example unsaturated C₁-C₆ acids, ethers, alcohols, aldehydes, ketones or esters, sugar units, alkoxy units, maleic anhydride and saturated polyalcohols such as glycerol. Preferably the hydrophobic side groups are composed of alkoxy groups for example butylene oxide and/or propylene oxide and/or alkyl or alkenyl chains having from 5 to 24 carbon atoms. The hydrophobic groups may be connected to the hydrophilic backbone via relatively hydrophilic bonds for example a poly ethoxy linkage.

Preferred polymeric carboxylate-containing builder compounds of this type are the polymers described in WO 91/ 08281.

Preferred counterions for the polymeric organic (carboxylate-containing) builder compounds are for example sodium, magnesium or calcium ions.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

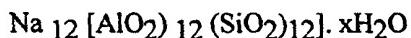
The builder system of the invention can comprise phosphate-containing builder material. It can however be preferred that the builder system is substantially free of phosphate-containing builders. Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

The builder system can also comprise silicate-containing builder compounds. Preferred are sodium silicates, preferably having a ratio of SiO₂:Na₂O = 2:1. Preferred can be, amorphous sodium silicate.

Other preferred silicate containing builder compounds are crystalline layered silicates, preferably sodium silicates. Preferred can be the crystalline layered silicate of formula δ -Na₂Si₂O₅, known as NaSKS-6 (Hoechst).

Other highly preferred builders comprised in the builder system of the invention are aluminosilicate zeolites which preferably have the unit cell formula Na_z[(AlO₂)_z(SiO₂)_y]. xH₂O, wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% by weight of the material of water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula:



wherein x is from 20 to 30, especially 27. Zeolite X has the formula Na₈₆[(AlO₂)₈₆(SiO₂)₁₀₆]. 276 H₂O.

Another preferred aluminosilicate zeolite is zeolite MAP builder.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal alumino-silicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

In a preferred aspect the zeolite MAP detergent builder has a particle size, expressed as a d_{50} value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres.

The d_{50} value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional analytical techniques such as microscopic determination using a scanning electron microscope or by means of a laser granulometer. Other methods of establishing d_{50} values are disclosed in EP 384070A.

Alkalinity system

The detergent compositions of the present invention preferably comprise up to 50% by weight, more preferably from 5% to 30%, more preferably from 8% to 20%, even more preferably from 10% to 15% by weight of the composition of an alkalinity system, comprising carbonate salts.

Examples of preferred carbonates are the alkaline earth and alkali metal carbonates, including sodium carbonate, bicarbonate and sesqui-carbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Alkali metal percarbonate salts may also be included in the alkalinity system of the detergent compositions and are also suitable carbonate and are described below in more detail.

Highly suitable carbonates can be anhydrous sodium carbonate. It can be preferred that the carbonate salts are comprised in particles of a particle size between 200 μm and 900 μm and anhydrous sodium bicarbonate with a particle size distribution between 400 μm and 1200 μm .

Additional Detergent Components

The detergent compositions in accord with the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition or component, and the precise nature of the washing operation for which it is to be used.

The compositions or components thereof, of the invention preferably contain one or more additional detergent components selected from other surfactants, bleaches, bleach catalysts, additional organic polymeric compounds, enzymes, suds suppressors, lime soap, dispersants, soil suspension and anti-redeposition agents soil releasing agents, perfumes, brightners, photobleaching agents and additional corrosion inhibitors.

Additional Detergent Surfactants

Optionally, additional surfactants, selected from the group consisting of anionic zwitterionic, ampholytic and amphoteric surfactants can be present.

The total amount of surfactants is preferably of from 1% to 95%, preferably 3% to 70%, more preferably 5% to 40%, even more preferably 10% to 30%, most preferably 12% to 25% by weight of the detergent composition.

A preferred aspect of the present invention is a granular detergent composition. One or more of the surfactants can be comprised in a base composition, containing optionally hydrophobic peroxyacid bleaching component and/or hydrophilic nonionic surface-active component. The base composition may be prepared by spray-drying and or dry-mixing/agglomeration, as described herein.

Anionic surfactant

The detergent composition of the present invention can comprise one or more additional anionic surfactants. Any anionic surfactant useful for detergative purposes is suitable. Examples include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), N-acyl sarcosinates. Resin acids and hydrogenated

resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

The anionic surfactant is preferably present at a level of 0.5% to 60%, preferably at a level of from 3% to 50%, more preferably of from 5% to 35%, most preferably from 6% to 20% by weight of the composition.

Anionic sulfate surfactant

Additional anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C₉-C₂₂ alkyl sulfates, more preferably the C₁₁-C₁₅ branched chain alkyl sulfates and the C₁₂-C₁₄ linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₁₀-C₁₈ alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₁₁-C₁₈, most preferably C₁₁-C₁₅ alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactant

Additional anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic

acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{C}(\text{OO}-\text{M}^+)$ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $\text{RO}-(\text{CHR}_1-\text{CHR}_2-\text{O})_x-\text{R}_3$ wherein R is a C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R₃ is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON(R¹)CH₂COOM, wherein R is a C₅-C₁₇ linear or branched alkyl or alkenyl group, R¹ is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Nonionic surfactants

When present in the detergent compositions of the invention, the nonionic surfactants are preferably present in low levels, preferably from 0.5% to 20%, more preferably from 1% to 15%, even more preferably from 1.5% to 8% by weight. The ratio of the nonionic surfactants, when present, to the surfactant system is preferably from 5:1 to 1:20, more preferably from 5:1 to 1:10, even more preferably from 1:1 to 1:10.

Alkoxylated Nonionic Surfactant

Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic Alkoxylated Alcohol Surfactant

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms or more preferably 9 to 15 with from 3 to 12 moles of ethylene oxide per mole of alcohol.

Nonionic Polyhydroxy Fatty Acid Amide Surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R²CONR¹Z wherein : R₁ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R₂ is a C₅-C₃₁ hydrocarbyl, preferably straight-chain C₅-C₁₉ alkyl or alkenyl, more preferably

straight-chain C₉-C₁₇ alkyl or alkenyl, most preferably straight-chain C₁₁-C₁₇ - alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycetyl.

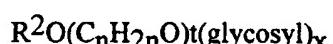
Nonionic Fatty Acid Amide Surfactant

Suitable fatty acid amide surfactants include those having the formula: R⁶CON(R⁷)₂ wherein R⁶ is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R⁷ is selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and -(C₂H₄O)_xH, where x is in the range of from 1 to 3.

Nonionic Alkylpolysaccharide Surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula:



wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Amphoteric Surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C₁₀-C₁₈ alkyl dimethylamine oxide, and C₁₀₋₁₈ acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic Surfactant

Zwitterionic surfactants can also be incorporated into the detergent in accord with the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, each R¹ is typically C₁-C₃ alkyl, and R² is a C₁-C₅ hydrocarbyl group. Preferred betaines are C₁₂₋₁₈ dimethyl-ammonio hexanoate and the C₁₀₋₁₈ acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Cationic Surfactants

Suitable cationic surfactants to be used in the detergent herein include the quaternary ammonium surfactants. Preferably the quaternary ammonium surfactant is a mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups. Preferred are also the mono-alkoxylated and bis-alkoxylated amine surfactants.

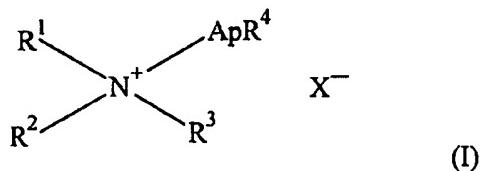
Another suitable group of cationic surfactants which can be used in the detergent compositions or components thereof herein are cationic ester surfactants. The cationic ester surfactant is a, preferably water dispersible, compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group.

Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

In one preferred aspect the ester linkage and cationically charged group are separated from each other in the surfactant molecule by a spacer group consisting of a chain comprising at least three atoms (i.e. of three atoms chain length), preferably from three to eight atoms, more preferably from three to five atoms, most preferably three atoms. The atoms forming the spacer group chain are selected from the group consisting of carbon, nitrogen and oxygen atoms and any mixtures thereof, with the proviso that any nitrogen or oxygen atom in said chain connects only with carbon atoms in the chain. Thus spacer groups having, for example, -O-O- (i.e. peroxide), -N-N-, and -N-O- linkages are excluded, whilst spacer groups having, for example -CH₂-O-CH₂- and -CH₂-NH-CH₂- linkages are included. In a preferred aspect the spacer group chain comprises only carbon atoms, most preferably the chain is a hydrocarbyl chain.

Cationic Mono-Alkoxylated Amine Surfactants

The cationic mono-alkoxyolated amine surfactant are preferably of the general formula I:

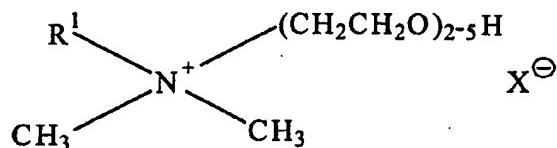


wherein R¹ is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, most preferably from about 6 to about 14 carbon atoms; R² and R³ are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl, most preferably both R² and R³

are methyl groups; R⁴ is selected from hydrogen (preferred), methyl and ethyl; X⁻ is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is a alkoxy group, especially a ethoxy, propoxy or butoxy group; and p is from 0 to about 30, preferably 2 to about 15, most preferably 2 to about 8, with the proviso that if A is ethoxy and R₄ is hydrogen and p is 1, R₁ is not a C₁₂-C₁₄ alkyl group.

Preferably the ApR^4 group in formula I has $p=1$ and is a hydroxyalkyl group, having no greater than 6 carbon atoms whereby the —OH group is separated from the quaternary ammonium nitrogen atom by no more than 3 carbon atoms. Particularly preferred ApR^4 groups are — $\text{CH}_2\text{CH}_2\text{OH}$, — $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, — $\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ and — $\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$, with — $\text{CH}_2\text{CH}_2\text{OH}$ being particularly preferred. Preferred R^1 groups have no greater than 10 carbon atoms, or even no greater than 8 or 9 carbon atoms. Preferred R^1 groups are linear alkyl groups. Linear R^1 groups having from 8 to 11 carbon atoms, or from 8 to 10 carbon atoms are preferred. Such a cationic surfactant which is highly preferred has a formula wherein R_1 is a C₈-C₁₀ alkyl group, p is 1, A is ethoxy and R_2 and R_3 are methyl groups.

Another highly preferred cationic mono-alkoxylated amine surfactants for use herein are of the formula



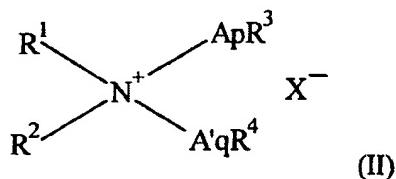
wherein R¹ is C₁₀-C₁₈ hydrocarbyl and mixtures thereof, especially C₁₀-C₁₄ alkyl, preferably C₁₀ and C₁₂ alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

As noted, compounds of the foregoing type include those wherein the ethoxy ($\text{CH}_2\text{CH}_2\text{O}$) units (EO) are replaced by butoxy, isopropoxy [$\text{CH}(\text{CH}_3)\text{CH}_2\text{O}$] and [$\text{CH}_2\text{CH}(\text{CH}_3\text{O})$] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

The levels of the cationic mono-alkoxylated amine surfactants used in detergent compositions of the invention is preferably from 0.1% to 20%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3.0% by weight of the composition.

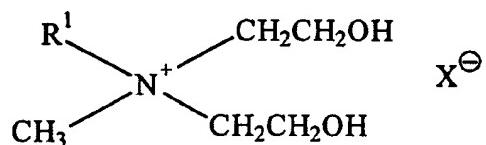
Cationic Bis-Alkoxylated Amine Surfactant

The cationic bis-alkoxylated amine surfactant preferably has the general formula II:



wherein R¹ is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R² is an alkyl group containing from one to three carbon atoms, preferably methyl; R³ and R⁴ can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X⁻ is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C₁-C₄ alkoxy, especially ethoxy, (i.e., -CH₂CH₂O-), propoxy, butoxy and mixtures thereof; p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

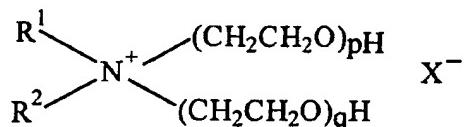
Highly preferred cationic bis-alkoxylated amine surfactants for use herein are of the formula



wherein R¹ is C₁₀-C₁₈ hydrocarbyl and mixtures thereof, preferably C₁₀, C₁₂, C₁₄ alkyl and mixtures thereof. X is any convenient anion to provide charge balance, preferably chloride. With reference to the general cationic bis-alkoxylated amine structure noted above, since in a preferred compound R¹ is derived from (coconut)

C₁₂-C₁₄ alkyl fraction fatty acids, R² is methyl and ApR³ and A'qR⁴ are each monoethoxy.

Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:



wherein R¹ is C₁₀-C₁₈ hydrocarbyl, preferably C₁₀-C₁₄ alkyl, independently p is 1 to about 3 and q is 1 to about 3, R² is C₁-C₃ alkyl, preferably methyl, and X is an anion, especially chloride or bromide.

Other compounds of the foregoing type include those wherein the ethoxy ($\text{CH}_2\text{CH}_2\text{O}$) units (EO) are replaced by butoxy (Bu) isopropoxy [$\text{CH}(\text{CH}_3)\text{CH}_2\text{O}$] and [$\text{CH}_2\text{CH}(\text{CH}_3\text{O})$] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

The levels of the cationic bis-alkoxylated amine surfactants used in detergent compositions of the invention is preferably from 0.1% to 20%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3.0% by weight of the composition.

Optional Surfactants

Suitable optional soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Other optional additional anionic surfactants are the carboxylate-based anionic surfactants known in the art and alkali metal sarcosinates of formula R-CON (R¹) CH₂ COOM, wherein R is a C₅-C₁₇ linear or branched alkyl or alkenyl group, R¹ is

a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts

Perhydrate Bleaches

An preferred additional components of the detergent is a perhydrate bleach, such as metal perborates, metal percarbonates, particularly the sodium salts. Perborate can be mono or tetra hydrated. Sodium percarbonate has the formula corresponding to 2Na₂CO₃.3H₂O₂, and is available commercially as a crystalline solid.

Potassium peroxyomonopersulfate, sodium per is another optional inorganic perhydrate salt of use in the detergent compositions herein.

Organic Peroxyacid Bleaching System

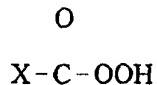
A preferred feature of detergent composition is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches, such as the perborate bleach of the claimed invention. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Peroxyacid Bleach Precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



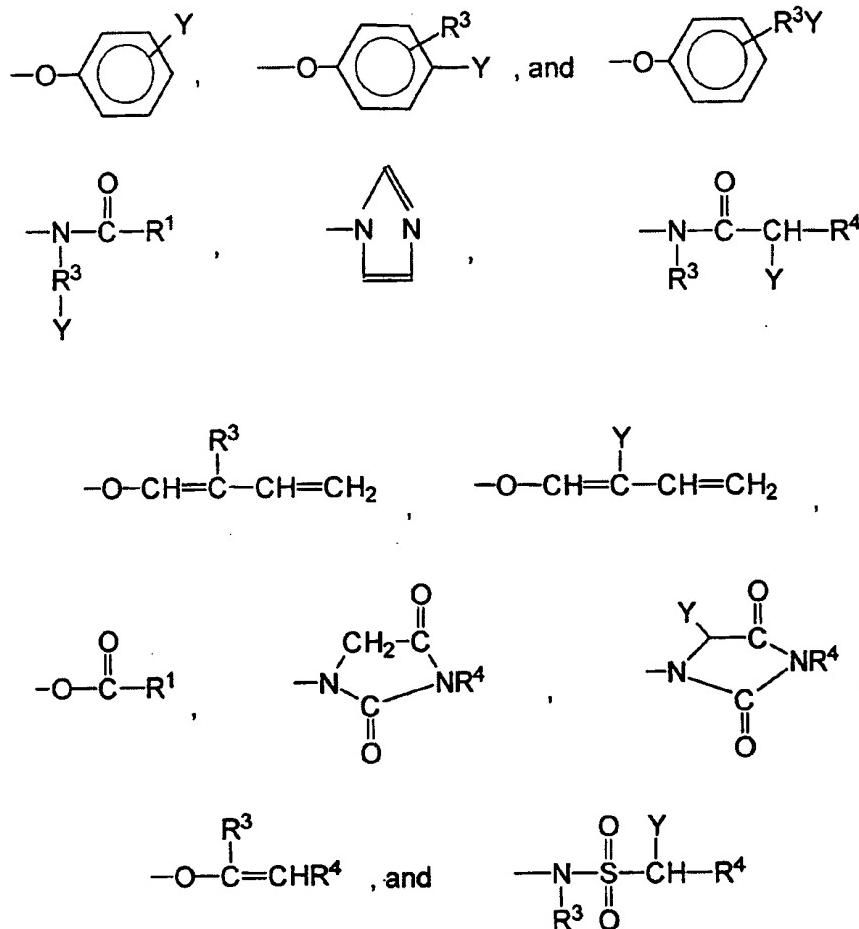
Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the detergent compositions.

Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Leaving Groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:



and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group. Any of R^1 , R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O<-N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted

ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Alkyl Percarboxylic Acid Bleach Precursors

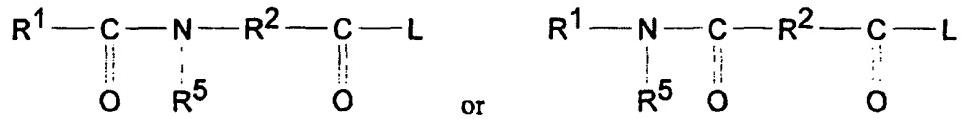
Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred. The TAED is preferably not present in the agglomerated particle of the present invention, but preferably present in the detergent composition, comprising the particle.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoxyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

Amide Substituted Alkyl Peroxyacid Precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein R¹ is an alkyl group with from 1 to 14 carbon atoms, R² is an alkylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Perbenzoic Acid Precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic Peroxyacid Precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter.

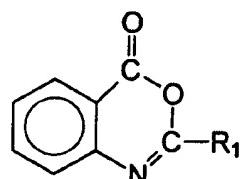
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

Benzoxazin Organic Peroxycid Precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

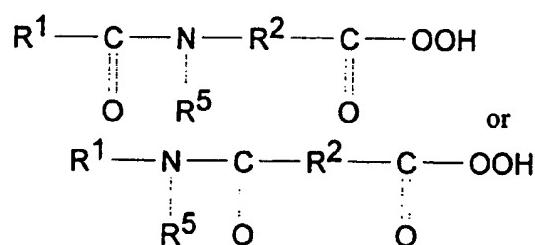


wherein R₁ is H, alkyl, alkaryl, aryl, or arylalkyl.

Preformed Organic Peroxvacid

The detergent composition may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R¹ is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diper oxytetradecanedioic acid and diper oxyhexadecanedioic acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Bleach Catalyst

The detergent composition can contain a transition metal containing bleach catalyst.

One suitable type of bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

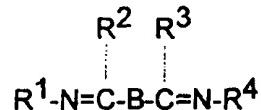
Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include Mn^{IV}₂(u-O)₃(1,4,7-trimethyl-1,4,7-triazacyclononane)₂-(PF₆)₂, Mn^{III}₂(u-O)₁(u-OAc)₂(1,4,7-trimethyl-1,4,7-triazacyclononane)₂-(ClO₄)₂, Mn^{IV}₄(u-O)₆(1,4,7-triazacyclononane)₄-(ClO₄)₂, Mn^{III}Mn^{IV}₄(u-O)₁(u-OAc)₂-(1,4,7-trimethyl-1,4,7-triazacyclononane)₂-(ClO₄)₃, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

The bleach catalysts useful herein may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear

manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)(OCH₃)₃-(PF₆).

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand. Said ligands are of the formula:



wherein R¹, R², R³, and R⁴ can each be selected from H, substituted alkyl and aryl groups such that each R¹-N=C-R² and R³-C=N-R⁴ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S, CR⁵R⁶, NR⁷ and C=O, wherein R⁵, R⁶, and R⁷ can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe,-bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include Co(2,2'-bispyridylamine)Cl₂, Di(isothiocyanato)bispyridylamine-cobalt (II), trisbipyridylamine-cobalt(II) perchlorate, Co(2,2-bispyridylamine)₂O₂ClO₄, Bis-(2,2'-bispyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including N₄Mn^{III}(u-O)₂Mn^{IV}N₄⁺ and [Bipy₂Mn^{III}(u-O)₂Mn^{IV}bipy₂]^{-(ClO₄)₃}.

Other bleach catalysts are described, for example, in European patent application, - publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

The bleach catalyst is typically used in a catalytically effective amount in the compositions and processes herein. By "catalytically effective amount" is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance bleaching and removal of the stain or stains of interest from the target substrate. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some users elect to use very hot water; others use warm or even cold water in laundering operations. Of course, the catalytic performance of the bleach catalyst will be affected by such considerations, and the levels of bleach catalyst used in fully-formulated detergent and bleach compositions can be appropriately adjusted. As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 1 ppm to about 200 ppm of the catalyst species in the wash liquor. To illustrate this point further, on the order of 3 micromolar manganese catalyst is effective at 40°C, pH 10 under European conditions using perborate and a bleach precursor. An increase in concentration of 3-5 fold may be required under U.S. conditions to achieve the same results.

Enzyme

Another preferred ingredient useful in the detergent is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α -amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of *Humicola* sp., *Thermomyces* sp. or *Pseudomonas* sp. including *Pseudomonas pseudoalcaligenes* or *Pseudomas fluorescens*. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Suds Suppressing System

The detergent compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali

metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkylamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises:

- (a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination
 - (i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and
 - (ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;
- (b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;
- (c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

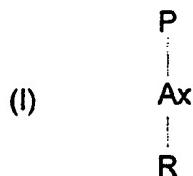
Polymeric Dye Transfer Inhibiting Agents

The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

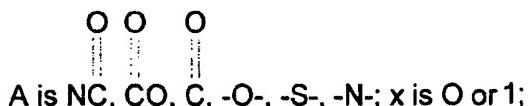
The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof, whereby these polymers can be cross-linked polymers.

a) Polyamine N-Oxide Polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :

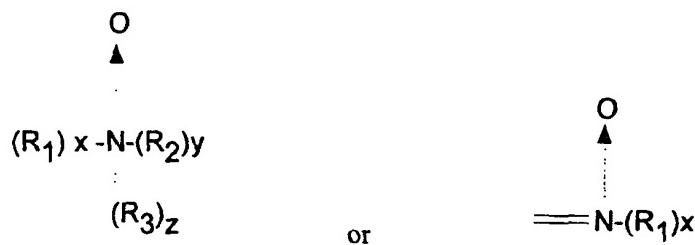


wherein P is a polymerisable unit, and



R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

b) Copolymers of N-Vinylpyrrolidone and N-Vinylimidazole

Suitable herein are copolymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

d) Polyvinyloxazolidone

The detergent compositions herein may also utilize polyvinyloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinyloxazolidones have an average molecular weight of from 2,500 to 400,000.

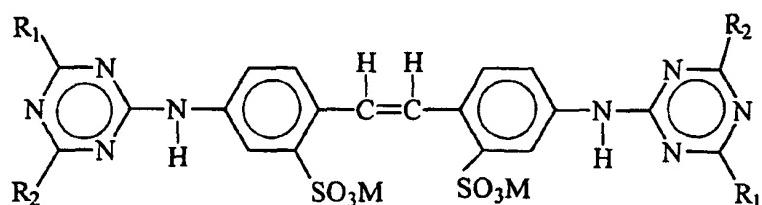
e) Polyvinylimidazole

The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical Brightener

The detergent compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species

is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Polymeric Soil Release Agent

Known polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present detergent compositions. If utilised, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly-

and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C₁-C₄ alkyl celluloses and C₄ hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Additional classes of SRA's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.;

Other Optional Ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include colours and filler salts, with sodium sulfate being a preferred filler salt.

Highly preferred compositions preferably contain from about 2% to about 10% by weight of an organic citric acid, preferably citric acid. Also preferably in combination with a carbonate salt, minor amounts (e.g., less than about 20% by weight) of neutralizing agents, buffering agents, phase regulants, hydrotropes, enzyme stabilizing agents, polyacids, suds regulants, opacifiers, anti-oxidants, bactericides, dyes, perfumes, such as those described in US Patent 4,285,841 to Barrat et al., issued August 25, 1981 (herein incorporated by reference), can be present in the compositions.

Form of the Compositions

The detergent composition of the invention can be made via a variety of methods, including dry-mixing and agglomerating of the various compounds comprised in the detergent composition.

The compositions in accordance with the invention can take a variety of physical solid forms such as tablet, flake, pastille and bar, and preferably granular forms.

Alternatively, the detergent compositions can be formulated such that they are chlorine-based bleach-compatible, thus ensuring that a chlorine based bleach can be added to the detergent composition by the user at the beginning or during the washing process.

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

The mid-chain branched surfactant system herein, preferably with additional surfactants, is preferably present in granular compositions in the form of surfactant agglomerate particles, preferably not comprising the bleach precursors, which may

take the form of flakes, prills, marumes, noodles, ribbons, but preferably take the form of granules. The most preferred way to process the particles is by agglomerating powders (e.g. aluminosilicate, carbonate) with high active surfactant pastes and to control the particle size of the resultant agglomerates within specified limits. Such a process involves mixing an effective amount of powder with a high active surfactant paste in one or more agglomerators such as a pan agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands, and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used, such as a Lodige CB (Trade Name).

A high active surfactant paste comprising from 50% by weight to 95% by weight, preferably 70% by weight to 85% by weight of the surfactants, including the mid-chain branched surfactants, is typically used. The paste may be pumped into the agglomerator at a temperature high enough to maintain a pumpable viscosity, but low enough to avoid degradation of the anionic surfactants used. An operating temperature of the paste of 50°C to 80°C is typical.

The mean particle size of the components of granular compositions in accordance with the invention, should preferably be such that no more than 25% of the particles are greater than 1.8mm in diameter and not more than 25% of the particles are less than 0.25mm in diameter. Preferably the mean particle size is such that from 10% to 50% of the particles has a particle size of from 0.2mm to 0.7mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of sieves, preferably Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The bulk density of the solid detergent compositions in accordance with the present is from 330 g/litre to 1240 g/litre, more preferably from 380g/litre to 1200 g/litre, most preferably from 420 g/litre to 850 g/ litre. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the

funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

Laundry Washing Method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 10g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred use aspect the detergent composition is formulated such that it is suitable for hand washing.

In another preferred aspect the detergent composition is a pre-treatment or soaking composition, to be used to pre-treat or soak soiled and stained fabrics.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C ₁₂ alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
C45AS	:	Sodium C ₁₄ -C ₁₅ linear alkyl sulfate

MES	:	-sulpho methylester of C ₁₈ fatty acid
CxyEzS	:	Sodium C _{1x} -C _{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
MBAS x,y	:	Sodium mid-chain branched alkyl sulfate having an average of x carbon atoms, whereof an average of y carbon atoms are comprised in (a) the branching unit(s).
C ₄₈ SAS	:	Sodium C ₁₄ -C ₁₈ secondary alcohol sulfate
SADE2S	:	Sodium C ₁₄ -C ₂₂ alkyl disulfate of formula 2-(R).C ₄ H ₇ -1,4-(SO ₄) ₂ where R = C ₁₀ 0C ₁₈ , condensed with z moles of ethylene oxide
C45E7	:	A C ₁₄ - ₁₅ predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
CxyEz	:	A C _{1x} - _{1y} branched primary alcohol condensed with an average of z moles of ethylene oxide
QAS II	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = 50%-60% C ₉ ; 40%-50% C ₁₁
QAS IV	:	R ₁ .N ⁺ (CH ₃)(C ₂ H ₄ OH) ₂ with R ₁ = C ₁₂ -C ₁₄
QAS V	:	R ² O(C ₂ H ₄ O) _x (glycosyl) ₂ , wherein R ² is a C ₈ -C ₁₀ alkyl group ; t is from 2 to 8
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
TPKFA	:	C ₁₂ -C ₁₄ topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate
Zeolite A	:	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (Al ₁₀ SiO ₂) ₁₂ .27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers
NaSKS-6	:	Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅
Carbonate	:	Anhydrous sodium carbonate with a particle size between 200μm and 900μm
Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
Silicate	:	Amorphous Sodium Silicate (SiO ₂ :Na ₂ O; 2.0 ratio)
Sodium sulfate	:	Anhydrous sodium sulfate
Citric acid	:	Anhydrous citric acid

Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a - particle size distribution between 425µm and q 850µm
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
MA/AA 2	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 3,000
MA/AA 3	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 12,000
AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
CMC	:	Sodium carboxymethyl cellulose
Protease	:	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
Alcalase	:	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
Cellulase	:	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
Amylase	:	Amyloytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
Lipase	:	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
Endolase	:	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
Percarbonate	:	Sodium Percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
NAC-OBS	:	(Nonanamido caproyl) oxybenzene sulfonate in the form of the sodium salt.
NOBS	:	Nonanoyl oxybenzene sulfonate in the form of the sodium salt
DPDA	:	Diperoxydodecanedioic acid
PAP	:	N-phthaloylamidoperoxicaproic acid
NAPAA	:	Nonanoylamido peroxy-adipic acid

NACA	:	6 nonylamino - 6 oxo - capronic acid.
TAED	:	Tetraacetylethylenediamine
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060.
Photoactivated	:	Sulfonated Zinc or aluminium Phthlocyanine encapsulated
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2,2'-disulfonate.
HEDP	:	1,1-hydroxyethane diphosphonic acid
PVNO	:	Polyvinylpyridine N-oxide
PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole
QEA	:	bis ((C ₂ H ₅ O)(C ₂ H ₄ O) _n) (CH ₃) -N ⁺ -C ₆ H ₁₂ -N ⁺ -(CH ₃) bis ((C ₂ H ₅ O)-(C ₂ H ₄ O) _n), wherein n=from 20 to 30
SRP 1	:	Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
SRP 2	:	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

In the following Examples all levels are quoted as parts per weight of the composition or % by weight of the composition, as indicated:

Example 1

The following high density granular laundry detergent compositions A to F of particular utility under European machine wash conditions were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	12.0	12.0	10	8.0	18.0	8.0

TAS	1.0	0	2.0	0	0	2.0	-
C25E9	3.4	-	-	3.4	5.4	2.4	
C25E7	-	3.0	4.5	-	-	-	
C46AS	2.0	2.0	-	-	-	4.0	
C24AS	-	-	5.0	5.0	4.0	0.5	
SADS	-	-	-	-	1.0	-	
MBAS 16.5, 1.7	6.0	3.0	8.0	10.5	4.0	2.0	
QAS II	-	-	0.8	-	-	0.8	
Zeolite A	10.1	5.7	8.0	12.0	16.0	18.1	
Carbonate	13.0	13.0	13.0	20.0	20.0	20.0	
Citric acid	2.0	1.0	2.0	-	-	-	
Silicate	1.4	1.4	1.4	3.0	3.0	1.0	
Sulfate	26.1	26.1	26.1	26.1	26.1	26.1	
MA/AA	0.3	2.0	-	-	-	-	
AA	-	-	-	0.5	2.0	-	
CMC	0.2	0.2	0.2	0.2	0.2	0.2	
PB4	9.0	9.0	9.0	-	-	-	
Percarbonate	-	-	-	18.0	15.0	20.0	
TAED	-	-	1.0	1.5	-	-	

NAC-OBS	4.0	2.5	0.5	1.0	2.0	5.0
DTPMP	0.25	0.25	0.25	0.25	0.25	0.25
EDDS	-	-	0.25	0.4	-	-
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
QEA	0.5	1.0	-	-	0.5	-
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.1	0.1	0.1	0.1
Photoactivated bleach (ppm)	15 ppm					
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Density in g/litre	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions G to I of bulk density 750. g/litre are compositions according to the invention:

	G	H	I
LAS	18.0	8.0	11.5
TAS	1.25	2.86	1.57
C45AS	3.5	3.24	2.0
C25AE3S	-	3.0	1.0

C45E7	3.25	-	-
C25E3	-	3.5	3.5
QAS I	0.8	2.0	-
MBAS 17, 1.5	7.0	10.0	5.0
STPP	10.5		
Zeolite A	-	12.0	5.0
NaSKS-6/silicate (79:21)	-	5.5	10.6
Citric acid/citrate	2.0	2.0	1.0
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	2.0	-	-
Sodium sulfate	10.0	-	7.0
PB4	5.0	12.7	-
TAED	0.5	0.2	-
NAC OBS	1.0	2.2	-
DTPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Protease	0.26	0.85	0.85

Lipase	0.15	0.15	0.15	-
Cellulase	0.28	0.28	0.28	
Amylase	0.1	0.1	0.1	
MA/AA	0.8	1.6	1.6	
CMC	0.2	0.4	0.4	
PVP	-	-	0.8	
Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm	
Brightener 1	0.08	0.19	0.19	
Brightener 2	-	0.04	0.04	
Perfume	0.3	0.3	0.3	
Silicone antifoam	0.5	2.4	2.4	
Minors/misc to 100%	n.a.	n.a.		

Example 3

The following are detergent formulations, according to the present invention where J is a phosphorus-containing detergent composition, K is a zeolite-containing detergent composition and L is a compact detergent composition:

	J	K	L	M
Blown Powder				
STPP	8.0	-	12.0	-
Zeolite A	-	14.0	-	7.0
C45AS	4.0	-	4.0	5.0
QAS I	-	1.0	-	-

MBAS 17, 1.5	4.0	11.0	10.0	6.0
SASDE2S	2.0	-	-	-
C ₂₅ AE ₃ S	-	1.0	-	1.0
MA/AA	-	1.0	-	1.0
MA/AA 2	2.0	-	1.0	-
LAS	14.0	2.0	3.0	1.6
TAS	-	4.0	2.0	-
Silicate	1.0	3.0	3.0	-
CMC	1.0	1.0	0.5	1.0
Brightener 2	0.2	0.2	0.2	0.2
Soap	1.0	-	-	1.0
DTPMP	0.4	0.4	0.2	0.4
Spray On				
C45E7	-	2.5	-	-
C25E3	2.5	-	4.0	1.5
Silicone antifoam	0.3	0.3	0.3	0.3
Perfume	0.3	0.3	0.3	0.3
Dry additives				
QEA	-	0.5	1.0	-
Carbonate	6.0	13.0	15.0	13.0
PB4	18.0	18.0	10.0	-
PB1	4.0	4.0	-	-
NOBS	3.0	4.2	1.0	-
Photoactivated bleach	0.02	0.02	0.02	0.02
Manganese catalyst	-	-	0.5	-
Protease	1.0	1.0	1.0	1.0
Lipase	0.4	0.4	0.4	0.4
Amylase	0.25	0.30	0.15	0.3
Dry mixed sodium sulfate	3.0	3.0	5.0	3.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0	100.0
Density (g/litre)	630	670	670	670

Example 4

The following are detergent formulations according to the present invention:

	N	O	P	Q
LAS	-	14.0	8.0	12.0
TAS	-	1.0	4.0	-
MBAS 16.5, 1.8	15.0	10.0	6.0	8.0
C45AS	4.0	4.0	6.0	6.0

MES	3.0	-	-	-
QAS II	0.4	-	1.0	-
TFAA	-	1.0	-	-
C25E5/C45E7/C ₂ E ₃	-	2.0	-	1.0
STPP	16.0	18.0	8.0	12.0
Silicate	2.0	1.0	5.0	6.0
Carbonate	13.0	7.5	4.0	5.0
Bicarbonate	-	7.5	-	-
DTPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.0	-	1.0
AA	-	-	2.0	-
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.15	0.05	-	/ -
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-
NACA	-	-	-	3.0
NAC OBS	2.0	1.0	0.9	3.1
Balance (Moisture and Miscellaneous)	100	100	100	100

Example 5

The following are detergent formulations according to the present invention:

	R	S	T
Blown Powder			
MBAS 16.5, 1.8	-	10.0	3.0
MBAS 17, 2.6	6.0	-	4.0
Zeolite A	8.0	12.0	6.0
Sodium sulfate	19.0	5.0	7.0
MA/AA	1.0	3.0	1.0
MES	-	5.0	-
LAS	10.0	9.0	13.5
C45AS	3.0	4.0	7.0

Silicate	-	1.0	1.0
Soap	-	-	2.0
Brightener 1	0.2	0.2	0.2
Carbonate	8.0	16.0	20.0
Spray On			
C45E5	1.0	1.0	-
Dry additives			
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NOBS	-	6.1	-
NAC OBS	-	-	4.5
Sodium sulfate	-	6.0	-
Balance (Moisture and Miscellaneous)	100	100	100

Example 6

The following are high density and bleach-containing detergent formulations according to the present invention:

	U	V	W
Blown Powder			
Zeolite A	-	7.0	10.0
Sodium sulfate	0.0	5.0	0.0
LAS	10.0	-	10.0
C45AS	3.0	2.0	4.0
QAS	-	-	1.5
DTPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
MBAS 6.5, 1.8	5.0	8.0	4.0
Agglomerates			
LAS	3.0	1.0	1.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	5.0	5.0
Carbonate	8.0	8.0	4.0
Spray On			
Encapsulated Perfume	0.3	0.3	0.3

	C25E3	2.0	-	2.0
Dry additives				
QEА	-	-	0.5	
Citrate	5.0	-	2.0	
Bicarbonate	-	3.0	-	
Carbonate	8.0	15.0	10.0	
NAC OBS	6.0	-	5.0	
Manganese catalyst	-	-	0.3	
NOBS	-	2.0	-	
PB1	14.0	7.0	10.0	
Polyethylene oxide of MW 5,000,000	-	-	0.2	
Bentonite clay	-	-	10.0	
Citric acid	-	1.0	0.5	
Protease	1.0	1.0	1.0	
Lipase	0.4	0.4	0.4	
Amylase	0.6	0.6	0.6	
Cellulase	0.6	0.6	0.6	
Silicone antifoam	5.0	5.0	5.0	
Dry additives				
Sodium sulfate	0.0	3.0	0.0	
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0	
Density (g/litre)	850	850	850	

Example 7

The following are high density detergent formulations according to the present invention:

	X	Y
Agglomerate		
MES	-	12.0
LAS	12.0	-
TAS	-	2.0
C45AS	6.0	4.0
MBAS16.5, 1.6	-	9.0
MBAS16.5, 2.8	10.0	-
Zeolite A	10.0	6.0
Carbonate	4.0	8.0
MA/AA	1.0	2.0
CMC	0.5	0.5

	DTPMP	0.4	0.4
Spray On			
C25E3	1.0	1.0	
Perfume	0.5	0.5	
Dry Adds			
HEDP	0.5	0.3	
SKS 6	5.0	6.0	
Citrate	-	1.0	
Citric acid	2.0	-	
NAC OBS	4.1	-	
TAED	0.8	2.0	
Percarbonate	20.0	20.0	
SRP 1	0.3	0.3	
Protease	1.4	1.4	
Lipase	0.4	0.4	
Cellulase	0.6	0.6	
Amylase	0.6	0.6	
QEA	1.0	-	
Silicone antifoam	5.0	5.0	
Brightener 1	0.2	0.2	
Brightener 2	0.2	-	
Density (g/litre)	850	850	

Example 8

The following granular detergent formulations are examples of the present invention.

	AH	AI	AJ
Blown powder			
MES	-	2.0	-
LAS	2.0	-	3.0
C45AS	-	1.0	-
C46AS	4.0	-	-
C45AE35	7.0	5.0	3.0
MBAS14.5, 1.7	8.0	-	-
Zeolite A	6.0	4.0	6.0
MA/AA 2	1.0	-	-
AA	1.0	2.0	1.0
Sodium sulfate	3.3	24.0	13.3
Silicate	1.0	2.0	1.0
Carbonate	9.0	15.0	8.0
QEA	0.4	-	0.5
PEG 4000	-	1.0	1.5

Brightener	0.3	0.3	0.3
Spray on			
C25E5	0.5	1.0	-
Perfume	0.3	1.0	0.3
Agglomerates			
C45AS	5.0	2.0	5.0
LAS	4.0	11.0	2.0
MBAS17, 2.0	15.0	6.0	-
Zeolite A	7.5	-	7.5
HEDP	1.0	-	2.0
Carbonate	4.0	-	4.0
PEG 4000	0.5	-	0.5
Misc (water etc)	2.0	-	2.0
Dry additives			
NOBS	4.0	-	-
TAED	-	-	2.0
PB4	1.0	-	2.0
Carbonate	5.3	-	2.5
Cumeme sulfonic acid	2.0	-	2.0
Lipase	0.4	0.1	0.05
Cellulase	0.2	-	0.2
Amylase	0.3	-	-
Protease	1.6	-	1.6
PVPVI	0.5	-	-
PVNO	0.5	-	-
SRP1	0.5	-	-
Silicone antifoam	0.2	-	0.2

Example 9

	AK	AL	AM	AN	AO	AP
C45AS	11.0	5.1	4.0	8.5	4.1	9.8
C25AES	1.3	1.0	-	1.3	1.0	-
LAS	9.4	6.6	23.5	3.7	1.7	4.3
C25E3/ C25E5	1.5	4.7	3.3	1.5	4.7	3.3
MBAS 16.5, 1.7	9.0	5.0	10.0	12.2	5.9	14.1
QAS	-	1.15	0.7	-	1.7	-
Zeolite A	16.0	10.7	8.0	7.7	16.7	10.0
SKS-6	-	9.0	6.0	-	3.0	5.0
Citric acid	-	1.5	-	-	1.5	-

MA/AA	-	0.6	-	-	0.6	--
MA/AA 3	-	-	3.0	-	-	2.0
AA	2.2	-	-	2.6	-	-
EDDS	-	0.3	-	-	0.3	-
HEDP	-	0.5	-	-	0.5	-
Carbonate	26.0	12.5	14.9	26.0	12.5	14.9
Silicate	0.8	0.8	3.0	0.8	0.8	3.0
PB1	1.0	-	3.9	1.0	-	3.9
NACA-OBS	-	2.75	-	-	2.7	-
PC	-	17.3	-	-	17.3	-
NOBS	-	2.7	4.0	-	-	4.0
TAED	-	3.5	-	-	3.5	-
Protease	0.26	0.3	0.2	0.6	0.3	0.2
Lipase	-	-	-	-	-	-
Cellulase	0.3	0.2	-	0.3	0.3	-
Amylase	-	0.3	-	-	0.3	-
Brightener	0.17	0.06	0.30	0.17	0.06	0.3
SRP1	0.41	0.2	0.5	0.41	0.2	0.5
PEG	1.6	-	0.19	1.6	-	0.19
Sulfate	5.8	6.4	3.0	5.5	6.0	3.8
CMC	-	0.5	-	-	0.5	-
MgSO ₄	-	0.13	-	-	0.13	-
Photobleach	-	0.0026	-	-	0.0026	-
Silicone anti-foam	0.02	0.21	0.17	0.02	0.21	0.17
Perfume	0.42	0.55	0.25	0.42	0.55	0.25

Example 10

The following laundry detergent compositions AQ to AT are prepared in accord with the invention:

	AQ	AR	AS	AT
MBAS 16.5, 1.7	22	16.5	11	5.5
C45 AS	8	10	11	4
C45E1S	4	3	-	1
LAS	8	14	-	4
C16 SAS	-	-	3	-
MES	-	-	12	-

C23E6.5	1.5	1.5	1.5	1.5
Zeolite A	7.0	10.0	12.0	14.0
AA	2.3	2.3	2.3	2.3
Carbonate	7.0	15.0	27.0	25.0
Silicate	0.6	0.6	0.6	0.6
Perborate	1.0	1.0	1.0	1.0
Protease	0.3	0.3	0.3	0.3
Cellulase	0.3	0.3	0.3	0.3
SRP1	0.4	0.4	0.4	0.4
Brightener	0.2	0.2	0.2	0.2
PEG	1.6	1.6	1.6	1.6
Sulfate	5.5	5.5	5.5	5.5
Silicone Antifoam	0.42	0.42	0.42	0.42
Moisture & Minors	---Balance---			
Density (g/L)	660	660	660	660

Example 11

The following laundry detergent compositions AU to AY are prepared in accord with the invention:

	AU	AV	AW	AX	AY
MBAS 16.5,1.7	14.8	16.4	12.3	8.2	4.1
C45 AS	5	7	6	4	12
C45E3S	2	-	4	-	5
LAS	14	8	-	18	5
C16 SAS	-	-	1	-	1
MES	-	-	10	-	-
TFAA	1.6	0	0	0	0
C24E3	4.9	4.9	4.9	4.9	4.9
Zeolite A	10	5	7	11	15
NaSKS-6	6	9	5	2.0	4.6
Citrate/citric	1.0	1.0	2.0	-	0.5
MA/AA	4.8	2.8	-	1.0	1.0
HEDP	0.5	0.5	0.5	0.5	0.5
Carbonate	8.5	8.5	8.5	8.5	8.5
PB1	13.0	-	15.0	-	-
Percarbonate	-	20.7	-	20.7	20.7
NACAOBS	4.0	3.0	1.0	-	-
TAED	-	-	4.8	4.8	4.8
QEA	1.0	1.0	-	-	-
QAS	1.0	-	-	-	1.0

Protease	0.9	0.9	0.9	0.9	0.9
Lipase	0.15	0.15	0.15	0.15	0.15
Cellulase	0.26	0.26	0.26	0.26	0.26
Amylase	0.36	0.36	0.36	0.36	0.36
SRP	0.2	0.2	0.2	0.2	0.2
Brightener	0.2	0.2	0.2	0.2	0.2
Sulfate	2.3	2.3	2.3	2.3	2.3
Silicone Antifoam	0.4	0.4	0.4	0.4	0.4
Moisture & Minors	---Balance---				
Density (g/L)	850	850	850	850	850

Example 12

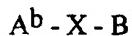
The following laundry detergent compositions AZ to Ee are prepared in accord with the invention:

	AZ	Aa	Bb	Cc	Dd	Ee
MBAS 16.5, 7.1	32	24	12	16	16	8
C45 AS	5	8	6.5	5.0	12.0	-
C45E1S	-	-	-	-	2.5	7.2
LAS	-	2.0	8	23	12	16
C16 SAS	1.0	-	-	-	-	-
MES	14	-	-	-	-	-
C23E6.5	3.6	3.6	3.6	3.6	3.6	3.6
QAS	-	0.5	-	-	0.5	-
Zeolite A	9.0	5.0	12.0	3.0	9.0	8.0
Polycarboxylate	2.0	5.0	3.0	7.0	6.0	5.0
Carbonate	18.4	18.4	18.4	18.4	18.4	18.4
Silicate	1.0	10	5.0	10	4.5	3.0
Perborate	3.9	3.9	3.9	3.9	3.9	3.9
NOBS	4.1	4.1	4.1	4.1	4.1	4.1
Protease	0.9	0.9	0.9	0.9	0.9	0.9
SRP1	0.5	0.5	0.5	0.5	0.5	0.5
Brightener	0.3	0.3	0.3	0.3	0.3	0.3
PEG	0.2	0.2	0.2	0.2	0.2	0.2
Sulfate	5.1	5.1	5.1	5.1	5.1	5.1
Silicone Antifoam	0.2	0.2	0.2	0.2	0.2	0.2
Moisture & Minors	---Balance---					
Density (g/L)	810	810	810	810	810	810

What is claimed is:

1. A solid detergent composition having a density of from 330 grams /litre to 1400 grams/ litre comprising

a) at least 0.5%, preferably at least 5%, more preferably at least 10% by weight of the composition of a surfactant system, comprising longer alkyl chain, mid-chain branched surfactant compounds of the formula:



wherein:

(I) A^b is a hydrophobic mid-chain branched alkyl moiety, having in total 9 to 22 carbons in the moiety, preferably from 12 to about 18, having: (1) a longest linear carbon chain attached to the - X - B moiety in the range of from 8 to 21 carbon atoms; (2) one or more $C_1 - C_3$ alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of the position 2 carbon, counting from position 1 carbon (#1) which is attached to the - X - B moiety, to the position of the terminal carbon minus 2 carbons, (the ($\omega - 2$) carbon); and (4) when more than one of these compounds is present, the average total number of carbon atoms in the A^b -X moieties in the above formula is within the range of greater than 14.5 to about 18, preferably from about 15 to about 17;

(II) B is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, preferably polyoxyethylene and polyoxypropylene, alkoxyolated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polygluconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccinimates, polyalkoxylated carboxylates, glucamides, taurinates, sarcosinates, glycinate, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxylated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkylated/polyhydroxyalkylated quats, alkylated quats,

alkylated/polyhydroxylated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and

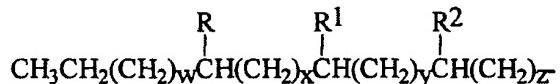
(III) X is selected from -CH₂- and -C(O)-; and

b) from 0.5% to 25% by weight of the composition a builder system; and

c) from 0.0% to 50% by weight of the composition of an alkalinity system comprising carbonate salts,

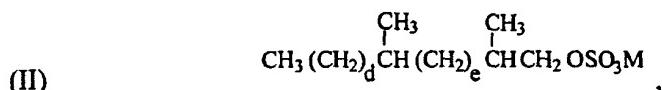
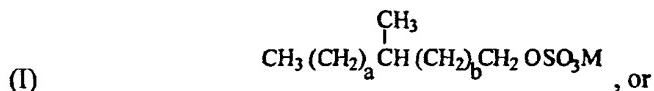
with the proviso that when system a) is present at a level of 3% by weight and system b) is present at a level of 19% by weight, the alkalinity system c) does not comprise 8% by weight of sodium carbonate.

2. A detergent composition according to claim 1 wherein the surfactant compounds of the surfactant system of a) are of the above formula wherein the A^b moiety is a branched primary alkyl moiety having the formula:



wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula, including the R, R¹, and R² branching, is from 13 to 19; R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl, preferably methyl, provided R, R¹, and R² are not all hydrogen and, when z is 0, at least R or R¹ is not hydrogen; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer from 0 to 13; and w + x + y + z is from 7 to 13.

3. A detergent composition according to claim 1 or 2 wherein the surfactant system a) comprises at least 20%, preferably at least 90% by weight of one or more mid-chain branched alkyl sulfates having the formula:



or mixtures thereof; wherein M represents one or more cations; a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8; when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9; when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10; when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11; when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12; when a + b = 15, a is an integer from 2 to 14 and b is an integer from 1 to 13; when a + b = 16, a is an integer from 2 to 15 and b is an integer from 1 to 14; when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6; when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7; when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8; when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9; when d + e = 12, d is an integer from 2 to 11 and e is an integer from 1 to 10; when d + e = 13, d is an integer from 2 to 12 and e is an integer from 1 to 11; when d + e = 14, d is an integer from 2 to 13 and e is an integer from 1 to 12; whereby the average total number of carbon atoms in the branched primary alkyl moieties is from 14.5 to 17.5.

4. A detergent composition according to any preceding claim wherein the surfactant compounds of the surfactant system of a) have a A^b - X moiety comprising from 16 to 18 carbon atoms and B is a sulfate group.
5. A detergent composition according to any preceding claim wherein the builder system comprises one or more builder material selected from amorphous silicates, crystalline layered silicates, aluminium silicates, polymeric or monomeric polycarboxylates and acids thereof and optionally phosphates.
6. A detergent composition according to any preceding claim wherein the builder system is substantially free of phosphate builder material.
7. A detergent composition according to any preceding claim wherein the level of the builder material is from 5% to 18% by weight of the composition.
8. A detergent composition according to any preceding claim wherein the alkalinity system comprises sodium carbonate present at a level of from 4% to 20% by weight.

9. A detergent composition according to any preceding claim whereby the density is from 550 grams/litre to 900 grams/litre.
10. A detergent composition according to any preceding claim wherein a nonionic surfactant, preferably a C₉₋₁₅ primary alcohol ethoxylate containing from 3-12 moles of ethylene oxide per mole of alcohol, is present at a ratio to the anionic surfactant of from 10:1 to 1:10, preferably 1:1 to 1:10.

INTERNATIONAL SEARCH REPORT

I | International Application No
PCT/US 97/18697

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/22 C11D1/00 C11D1/14 C11D17/06 C11D3/10

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 97 38956 A (CONNOR DANIEL STEDMAN ; PROCTER & GAMBLE (US)) 23 October 1997 see example 1C ----	1-10
E	WO 97 39088 A (CONNOR DANIEL STEDMAN ; VINSON PHILLIP KYLE (US); WILLMAN KENNETH W) 23 October 1997 see example 6E ----	1
A	DATABASE WPI Section Ch, Week 8238 Derwent Publications Ltd., London, GB; Class A97, AN 82-80582E XP002066464 & JP 57 133 200 A (KAO SOAP CO LTD) see abstract -----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

National Application No

PCT/US 97/18697

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